VIII. *The Liquefaction and Solidification of Argon.*

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Communicated by Professor WILLIAM RAMSAY, *F.R.S.*

HAVING been furnished, by Professor RAMSAY's kindness, with a sample of the new gas, argon, I have carried out experiments on its behaviour at low temperatures and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon sent by Professor RAMSAY amounted to 300 cub. centims. It was contained in a hermetically-sealed glass bulb, so constructed that it could easily be transferred, with no appreciable loss, into the carefully-dried and vacuous apparatus in which the proposed experiments were to be performed. The argon with which I was supplied had, according to Professor RAMSAY's statement, been dried with phosphoric anhydride; its density was 19·9 (H = 1); and he thought that at the outside it might contain 1 to 2 per cent. of nitrogen, although it showed no nitrogen spectrum when examined in a PLÜCKER's tube.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as of measuring its vapour pressure at several other low temperatures, while two other series served to determine its boiling- and freezing-points under atmospheric pressure, as well as its density at its boiling-point.

A detailed description of these experiments will be given in another place : I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a CAILLETET's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of CAILLETET's apparatus was so arranged that the portion immersed in the liquid ethylene had comparatively thin walls (not exceeding 1 millim.), so as to equalize the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both

ends with glass stop-cocks. By connecting the lower end of the burette with a mercury reservoir, the argon was transferred into a narrow doubly bent glass tube connected with the upper end of the burette, and in which the argon was liquefied, and
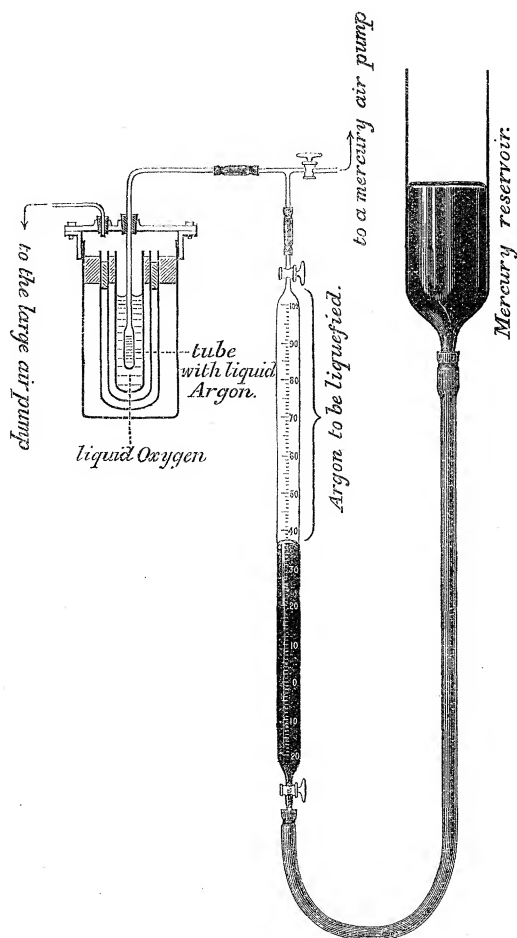
its volume in the liquid state measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

Determination of the Critical Constants of Argon.

As soon as the temperature of the liquid ethylene had been lowered to − 128°·6, the argon easily condensed to a colourless liquid under a pressure of 38 atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished at the following temperatures and corresponding pressures :—

Experiment.	Temperature.	Pressure.
	°	atmos.
1	− 121·2	50·6
2	− 121·6	50·6
3	− 120·5	50·6
4	− 121·3	50·6
5	− 121·4	50·6
6	− 119·8	50·6
7	− 121·3	50·6

In all seven determinations the critical pressure was found to be 50·6 atmospheres; but determinations of the critical temperature show slight differences. In experiments Nos. 3 and 6 less liquid argon was present in the tube than in the other five; in these the volume of liquid exceeded the volume of gas.

In determining the vapour pressures of argon, a tabular record of which is given below, I noticed slight differences of pressure according as I produced more or less of the liquid at the same temperature. This proved that the sample of argon contained an inconsiderable admixture of another gas, more difficult to liquefy; it is doubtless the trace of nitrogen previously referred to. The mean of the seven estimations of the critical temperature is − 121°, and this may be taken as the critical temperature of argon.

At lower temperatures the following vapour-pressures were recorded :—

Experiment.	Temperature.	Pressure.	Experiment.	Temperature.	Pressure.
	°	atmos.		°	atmos.
8	−128·6	38·0	13	−134·4	29·8
9	−129·6	35·8	14	−135·1	29·0
10	−129·4	35·8	15	−136·2	27·3
11	−129·3	35·8	16	−138·3	25·3
12	−129·6	35·8	17	−139·1	23·7

In Experiments Nos. 9, 10, and 17 the quantity of liquefied argon was very small, for it filled the tube only to a height of 3 to 5 millims., and in the other experiments the column of liquid argon was 20 millims. or more.

Determination of the Boiling- and Freezing-Points.

Two hundred cub. centims. of liquid oxygen, prepared in my large apparatus,[*] was poured into a glass vessel with quadruple walls, so as to isolate the liquid from

[*] 'Bulletin International de l'Académie de Cracovie,' June, 1890; also WIEDEMANN's 'Beiblätter,' vol. 15, p. 29.

external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about 70 cub. centims., boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature ($- 182°\cdot7$*) on admitting argon, no appearance of liquefaction could be noticed, even when compressed by increasing the atmospheric pressure by a quarter. This shows that its boiling-point lies below that of oxygen. But on diminishing the temperature of the liquid oxygen below $- 187°$, the liquefaction of the argon became manifest. When liquefaction had taken place, I carefully equalised the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling-point of argon under atmospheric pressure. Four experiments gave the numbers: $- 186°\cdot7$, $- 186°\cdot8$, $- 187°\cdot0$, and $- 187°\cdot3$. The mean is $- 186°\cdot9$, which I consider to be the boiling-point under atmospheric pressure (740·5 millims.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure, was 99·5 cub. centims.; the quantity of liquid corresponding to that volume of gas was approximately 0·114 cub. centim. Hence the density of argon at its boiling-point may be taken as approximately 1·5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given cannot lay claim to great exactness; yet they prove that the density of liquid argon at its boiling-point ($- 187°$) is much higher than that of oxygen, which I have found, under similar conditions, to be 1·124.

By lowering the temperature of the oxygen to $- 191°$ by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting-point gave the numbers: $- 189°\cdot0$, $- 190°\cdot6$, $- 189°\cdot6$, and $- 189°\cdot4$. The mean of these numbers is $- 189°\cdot6$; and this may be accepted as the melting-point of argon.

In the following table I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

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* I have re-determined the boiling-point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is 1°·3 lower than that which I previously recorded.

Name.	Critical tempera- ture.	Critical pressure.	Boiling point.	Freezing point.	Freezing pressure.	Density of gas.	Density of liquid at boiling point.	Colour of liquid.
		Atmos.	°	°	millims.			
Hydrogen (H$_2$) . .	{ Below. −220·0	} 20·0	?	?	?	1 0	?	Colourless
Nitrogen (N$_2$) . .	−146·0	35·0	−194·4	−214·0	60	14·0	0·885	,,
Carbonic oxide (CO)	−139·5	35·5	−190·0	−207·0	100	14 0	?	,,
Argon (A$_1$) . . .	−121·0	50·6	−187·0	−189·6	?	19·9	{ About 1·5 }	} ,,
Oxygen (O$_2$) . . .	−118·8	50·8	−182·7	?	?	16·0	1·124	Bluish
Nitric oxide (NO) .	− 93·5	71·2	−153·6	−167·0	138	15·0	?	Colourless
Methane (CH$_4$) . .	− 81·8	54·9	−164·0	−185·8	80	8·0	0·415	,,

As can be seen from the foregoing table, argon belongs to the so-called " permanent " gases, and, as regards difficulty in liquefying it, it occupies the fourth place, viz., between carbon monoxide and oxygen. Its behaviour on liquefaction places it nearest to oxygen, but it differs entirely from oxygen in being solidifiable ; as is well known, oxygen has not yet been made to assume a solid state

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling-point seem to have some relation to its simple molecular constitution.

NOTE ON A COMPARISON OF THE VAPOUR-PRESSURES OF ARGON WITH THOSE OF OTHER SUBSTANCES.

By WILLIAM RAMSAY *and* SYDNEY YOUNG.

The vapour-pressures of a considerable number of substances have been determined from low temperatures to the critical points, but as the critical pressure of argon is somewhat high, the boiling-points of very few are available for comparison through the whole range of equal pressures.

The critical pressure of benzene is so slightly below that of argon that the extra-polation of the vapour-pressure curve through the few degrees necessary to afford a comparison at the critical pressure of the new element is justifiable.

The other two substances chosen are ethyl alcohol and oxygen ; the second is interesting, as its vapour-pressures, like those of argon, have been determined by Professor OLSZEWSKI.

In the following table the boiling-points—on the absolute scale—of argon, benzene,

ethyl alcohol, and oxygen, are given at the pressures at which observations have been made with the first of these substances.

BOILING-Points on Absolute Scale.

Pressure in millims.	Argon.	Benzene.	Ethyl alcohol.	Oxygen.
740·5	86·1	352·5	350·65	90·1
18010	133·9	507·8	462·6	136·1
19230	134·7	512·5	465·8	137·4
20750	136·8	518·0	469·6	139·0
22040	137·9	522·3	472·7	140·2
22650	138·6	524·3	474·0	141·4
27210	143·5	538·3	483·7	145·0
28880	144·4	543·0	487·0	146·5
38460	152·0	565·9	503·1	153·7

The ratios of the absolute temperatures of argon to each of the other substances were calculated and plotted against the centigrade temperatures of the latter. Straight lines were then drawn to pass as well as possible through the points, and the following formulæ for the ratios were obtained :—

$$\frac{Argon}{Benzene} \qquad R' = ·2351 + ·0001155\, t \; (t = \text{temperature centigrade of benzene}).$$

$$\frac{Argon}{Ethyl\ Alcohol} \qquad R' = ·2164 + ·0003765\, t \; (t = \text{temperature centigrade of ethyl alcohol}).$$

$$\frac{Argon}{Oxygen} \qquad R' = ·9518 + 000522\, (t + 190) \; (t = \text{temperature centigrade of oxygen}).$$

The ratios calculated from the boiling-points and those given by the above formulæ are compared in the following table :—

Pressure in millims.	Ratios.					
	Argon/Benzene.		Argon/Alcohol.		Argon/Oxygen.	
	From boiling-points.	From formula.	From boiling-points.	From formula.	From boiling-points.	From formula.
740·5	·2443	·2443	·2455	·2456	·9556	·9555
18010	·2637	·2622	·2894	·2878	·9838	·9795
19230	·2628	·2628	·2892	·2890	·9804	·9802
20750	·2641	·2634	·2913	·2904	·9842	·9810
22040	·2640	·2639	·2917	·2916	·9836	·9817
22650	·2644	·2641	·2924	·2921	·9802	·9823
27210	·2666	·2657	·2967	·2957	·9896	·9842
28880	·2659	·2663	·2965	·2970	·9857	·9850
38460	·2686	·2689	·3021	·3030	·9889	·9887

Assuming the boiling-points of benzene, alcohol, and oxygen to be correct, those of argon could be calculated from them by multiplying the absolute temperatures of each substance by the corresponding ratio at each pressure.

The observed and re-calculated absolute temperatures of argon and the differences are given below :—

Pressure in millims.	Boiling-points (absolute) of argon.						
	Observed.	From benzene.	Δ.	From alcohol.	Δ.	From oxygen.	Δ.
740·5	86·1	86·1	0	86·1	0	86·1	0
18010	133·9	133·1	−0·8	133·1	−0·8	133·3	−0·6
19230	134·7	134·7	0	134·6	−0·1	134·7	0
20750	136·8	136·4	−0·4	136·4	−0·4	136·4	−0·4
22040	137·9	137·8	−0·1	137·8	−0·1	137·6	−0·3
22650	138·6	138·5	−0·1	138·5	−0·1	138·9	+0·3
27210	143·5	143·0	−0·5	143·0	−0·5	142·7	−0·8
28880	144·4	144·6	+0·2	144·6	+0·2	144·3	−0·1
38460	152·0	152·2	+0·2	152·4	+0·4	152·0	0

The comparison would, of course, be more valuable if there were some observations between 740 and 18,000 millims., but, so far as it goes, it will be seen that there is a very fair agreement between the observed temperatures and those calculated from the smoothed ratios.

It is hardly likely, though not impossible, that so good an agreement would be obtained with a mixture or an impure substance. It is, at any rate, certain that a distinct want of agreement would have shown that the argon was not a definite, pure substance, and the results may be taken as affording additional confirmation of the conclusion that argon is a definite, hitherto unknown constituent of the atmosphere, and that it has been isolated in a state very closely approaching to purity.